

# Mathematical Modelling for Water-Gas-Shift Converters

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**Abstract :** The application of Water-Gas-Shift (WGS) converters are growing in the industry due to the increase of hydrogen demand. Water-Gas-Shift reaction, which is essentially converting toxic carbon monoxide and steam into carbon dioxide and hydrogen, is a major component in the steam reforming process. There are a lot of researches and literatures into the catalysts and reaction kinetics. A mathematical model for such reactor will show the conversion alone the reactor and its concentration profile, which can be used for calculating catalysts weight and reactor sizes, it can also be used for process optimization.

**Keywords:** Packed bed Reactor, Modelling, Water-Gas-Shift.

## 1. Introduction

The application of Water-Gas-Shift (WGS) converters are growing in the industry due to the increase of hydrogen demand. Most WGS converters are used in anhydrous ammonia production and fertilizer usage [i] which is a huge market for hydrogen [ii]. There are also some recent innovations for hydrogen fuel cells which would also increase the market for a WGS. The hydrogen is produced by steam reforming of methane. After the reforming process, most methane will be converted into hydrogen and carbon dioxide, however, there will be some residual carbon monoxide left unreacted, in order to further improve the yield of hydrogen, WGS converters are introduced.

Due to the exothermal nature of the reaction, in order to achieve a desired conversion with a sufficient reaction rate, generally, two WGS converters are used: High temperature WGS and Low temperature WGS. The major amount of carbon monoxide is converted in the high temperature shift reactor which has a relatively fast reaction rate and the remaining will be removed by the low temperature shift reactor in order to achieve a high yield. With this design, both a high production rate and a high yield can be achieved. For different operating temperature, different catalysts will be used, common choices are iron-chromium based catalysts for the high temperature WGS [iii]. However, even though that this type of catalysts is well developed and widely used commercially, the EU legislation tend to restrict its usage due to its toxicity and the carcinogenic nature of chromium [iv]. Copper based catalysts are generally used for the low temperature WGS [v].

In addition, a combination of two reactors or a multistage reactor requires significantly less amount of steam to reach the same conversion. The efficiency of the conversion can also be increased by removing CO<sub>2</sub>, which can be done by membrane reactors [vi], although this is rarely practiced in reforming plants [i].

## 2. Method

A fixed bed reactor will be used for the WGS converter, and it is assumed to behave like a plug flow reactor [vii]. Therefore, the mass and energy balance can be carried out. But first, there are some assumptions to be made.

Assumptions:

- This operation works continuously, which means there is no accumulation in the system.
- There is no radial variance in this system, and the velocity profile will be a flat line. Therefore a 1-Dimension model can be developed.
- The reactor works under adiabatic conditions which means that there is no heat input nor exchange with its surroundings (perfect isolation).
- There is no Rate of work be done by the system.
- The reactor works under condition with a relative high temperature and pressure (30Bara), which is assumed that ideal gas law applies.
- There is no pressure drop along the column, this is justified using the short cut method.

### 2.1 Mass Balance

A mass balance will be derived from the first principle.[viii]

$$\left\{ \begin{array}{l} \text{Molar flow} \\ \text{into the} \\ \text{system} \end{array} \right\} + \left\{ \begin{array}{l} \text{Molar flow} \\ \text{out of} \\ \text{the system} \end{array} \right\} \pm \left\{ \begin{array}{l} \text{The rate of} \\ \text{generation} \\ \text{/consumption} \end{array} \right\} = \{ \text{Accumulation} \} \quad (2.1)$$

Since there is no accumulation in the fixed bed reactor, the mass balance can be written as,

$$F_A|V - F_A|(V + \Delta V) = (-r_A) * \Delta V \quad (2.2)$$

Divide by the control volume,

$$\frac{F_A|V - F_A|(V + \Delta V)}{\Delta V} = (-r_A) \quad (2.3)$$

When  $\Delta V$  goes infinitely small (i.e. when  $\Delta V$  tends to 0),

$$\frac{dF_A}{dV} = (-r_A) \quad (2.4)$$

Introducing the conversion term,

$$\frac{dF_{A0}*(1-X)}{dV} = (-r_A) \quad (2.5)$$

The final differential equation can be written as

$$-\frac{dX}{dV} = \frac{(-r_A)}{F_{A0}} \quad (2.6)$$

The rate equation can be changed into:

$$-\frac{dX}{dV} = \frac{(-r_A)*\rho_b}{F_{A0}} \quad (2.7)$$

Rearrange this equation, the differential equation can be written as conversion versus weight of catalysts.

$$-\frac{dX}{dW} = \frac{(-r_A)}{F_{A0}} \quad (2.8)$$

### 2.2 Energy Balance[viii]

$$\begin{aligned}
 & \left\{ \begin{array}{l} \text{Rate of flow} \\ \text{of heat to} \\ \text{the system} \\ \text{from the} \\ \text{surroundings} \end{array} \right\} - \left\{ \begin{array}{l} \text{Rate of work} \\ \text{done by} \\ \text{the system} \\ \text{on the} \\ \text{surroundings} \end{array} \right\} + \\
 & \left\{ \begin{array}{l} \text{Rate of energy} \\ \text{added to the} \\ \text{system by mass} \\ \text{flow into} \\ \text{the system} \end{array} \right\} - \left\{ \begin{array}{l} \text{Rate of} \\ \text{energy leaving} \\ \text{system by mass} \\ \text{flow out of} \\ \text{the system} \end{array} \right\} = \\
 & \left\{ \begin{array}{l} \text{Rate of} \\ \text{Accumulation} \\ \text{of energy} \\ \text{Within the} \\ \text{system} \end{array} \right\} \quad (2.9)
 \end{aligned}$$

$$Q - W + \sum(F_A * H_R)|z - \sum(F_A * H_R)|z + \Delta z = \frac{dE_{sys}}{dt} \quad (2.10)$$

Since there is no heat input of the system (adiabatic condition), there is also no work done to the system, therefore the term  $Q$  and  $W$  can be neglected.

$$\sum(F_A * H_R)|V - \sum(F_A * H_R)|V + \Delta V = 0 \quad (2.11)$$

Rearrange,

$$\frac{(F_A * H_R)|V - (F_A * H_R)|V + \Delta V}{\Delta V} = 0 \quad (2.12)$$

When  $\Delta V$  goes infinitely small (i.e. when  $\Delta V$  tends to 0),

$$\frac{d(F_A * H_R)}{dV} = 0 \quad (2.13)$$

Expand the differential term,

$$\left( H_R * \frac{dF_A}{dV} + F_A * \frac{dH_R}{dV} \right) = 0 \quad (2.14)$$

From Equation 2.5  $\frac{dF_A}{dV} = (-r_A)$ ,

$$\left( H_R * (-r_A) + F_A * \frac{dH_R}{dV} \right) = 0 \quad (2.15)$$

The rate of reaction is defined as follow, [ix]

$$Q = \sum H_{out} - \sum H_{in} = H_r \quad (2.16)$$

And the enthalpy is defined as

$$H = H_f^\circ + \int_{T_1}^{T_2} C_{p_i} dT \quad (2.17)$$

The values for heat capacity at various temperature and heat of formation can be found in ÇENGEL, Y. A., & BOLES, M. A. (2001)[x] and PERRY, R. H., & GREEN, D. W. (2008) [xi]. Differentiate with respect to temperature and re-arrange,

$$\frac{dH_R}{dV} = \sum C_{p_i} * \frac{dT}{dV} \quad (2.18)$$

$$\left( H_R * (-r_A) + \sum(C_{p_i} * F_i) * \frac{dT}{dV} \right) = 0 \quad (2.19)$$

$$-H_R * (-r_A) = \sum(C_{p_i} * F_i) * \frac{dT}{dV} \quad (2.20)$$

$$\frac{dT}{dV} = \frac{-H_R * (-r_A)}{\sum(C_{p_i} * F_i)} \quad (2.21)$$

Rearrange the equation:

$$\frac{dT}{dW} = \frac{-H_R * (-r_A)}{\sum(C_{p_i} * F_i)} \quad (2.22)$$

There are researches into the rate expression, there are some very detailed research papers into the reaction kinetics and its expression, there is a review paper written by Byron Smith R J, Muruganandam Loganathan, and Murthy Shekhar Shantha in 2010 [xii]. In this mathematical model, the rate expression was found in Rase, Howard F (1977) [xiii], the following empirical equation can be used to calculate the rate of reaction for WGS converters.

$$-r_{CO} = \frac{\psi_k \left( y_{CO} y_{H_2O} - \frac{y_{CO_2} y_{H_2}}{K_p} \right)}{379 * \rho_b} \quad (2.23)$$

This rate equation has a unit of  $mol kg^{-1} s^{-1}$ . A more detailed derivation of the rate equation can be found from Yogesh. J. Morabiya & Jalpa. A. Shah (2012) [xiv].

The rate constant can be calculated using the following equation: [xiii]  
Iron Catalyst: Unit of  $lbmol ft^{-3} hr^{-1}$

$$k = \exp \left( 15.95 - \frac{8640}{T} \right) \quad T \text{ in Rankins},$$

or,

$$k = \exp \left( 15.95 - \frac{4900}{T} \right) \quad T \text{ in Kelvin} \quad (2.24)$$

Copper Catalyst: Unit of  $lbmol ft^{-3} hr^{-1}$

$$k = \exp \left( 12.88 - \frac{3340}{T} \right) \quad T \text{ in Rankins}, \text{ or},$$

$$k = \exp \left( 12.88 - \frac{1855.5}{T} \right) \quad T \text{ in Kelvin} \quad (2.25)$$

Notice that the temperature is in unit of Rankins, a degree of Kelvin must be converted first before using this equation. In addition, the unit for the rate constant will be converted into  $mol m^{-3} s^{-1}$ .

The activity factor can also be obtained, [xiii], for pressure over 20 atm, the activity factor for iron catalyst will be 4, for pressure over 24.8 atm, the activity factor for copper-zinc catalyst will be 4.33.

Table 2.1 and Table 2.2 are the inlet composition calculated using Kinetic Equilibrium Constant, the data can be found from Martyn V. Twigg (1989) [xv].

**Table 2.1 Assumed Input for High Temperature WGS converter (Molar Unit)**

Molar Balance	kmol/s
Component	Input
CH <sub>4</sub>	<b>0.00515497</b>
H <sub>2</sub> O	<b>1.06077387</b>
CO	<b>0.30157525</b>
CO <sub>2</sub>	<b>0.16346733</b>
H <sub>2</sub>	<b>1.28312411</b>
N <sub>2</sub>	<b>0.51062092</b>
Ar	<b>0.00615055</b>
Total	<b>3.330867</b>

**Table 2.2 Assumed Input for Low Temperature WGS converter (Molar Unit)**

Molar Balance	kmol/s
Component	Input
CH <sub>4</sub>	<b>0.00515497</b>
H <sub>2</sub> O	<b>0.84917947</b>
CO	<b>0.08998085</b>
CO <sub>2</sub>	<b>0.37506173</b>
H <sub>2</sub>	<b>1.49471851</b>
N <sub>2</sub>	<b>0.51062092</b>
Ar	<b>0.00615055</b>
Total	<b>3.330867</b>

After all the derivations and information above, a mathematical modelling can be developed using MatLab, the results are shown in the following section.

### 3. Results and discussion

#### 3.1 High Temperature WGS converter

For High Temperature WGS converters, the results are presented as follow.

With this coding, by changing the feeding temperature, the conversion and weight of catalyst will change respectively. A change of 10°C in the feeding temperature is introduced, and the results are shown in figure 3.1 and 3.2.

Figure 3.1 shows the temperature profile in the reactor with different initial feed temperature. With a low feeding temperature, the rate of increase of temperature is small and the equilibrium temperature is lower, however, it takes more catalysts which means a bigger reactor and longer residence time to reach equilibrium. Increasing the feeding temperature, the temperature increase accelerates which means it reaches equilibrium much quicker; with a higher temperature, a lower amount of catalysts is required and the reactor size will be small which can save a lot catalysts and equipment costs. However, the materials for the reactor may have to change with a higher temperature.

Figure 3.2 shows the conversion of CO in the High temperature WGS converters with the weight of the catalysts. Same with the temperature profile, the higher the feeding temperature, the quicker it reaches equilibrium, however, the conversion of CO decreases with the increasing in temperature. This is mainly due to the nature of exothermal reaction. Therefore, compromises will have to be made when choosing the feed temperature.

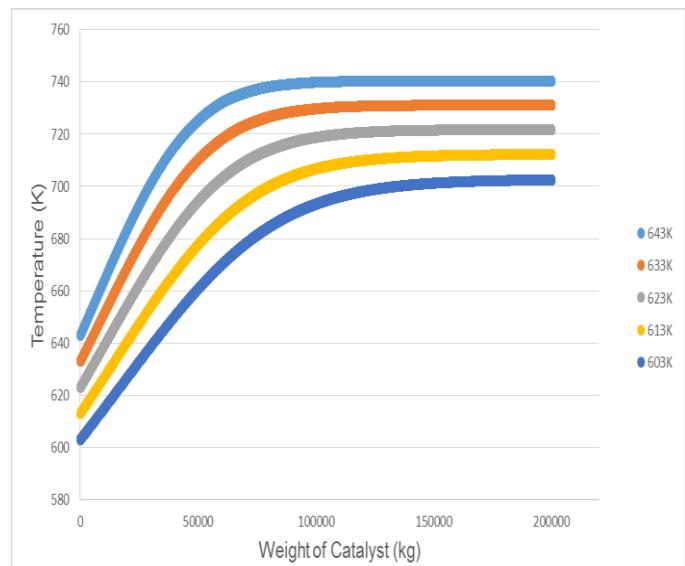


Figure 3.1 Temperature profile in the High temperature WGS converter, changing with the weight of catalyst with different feeding temperature.

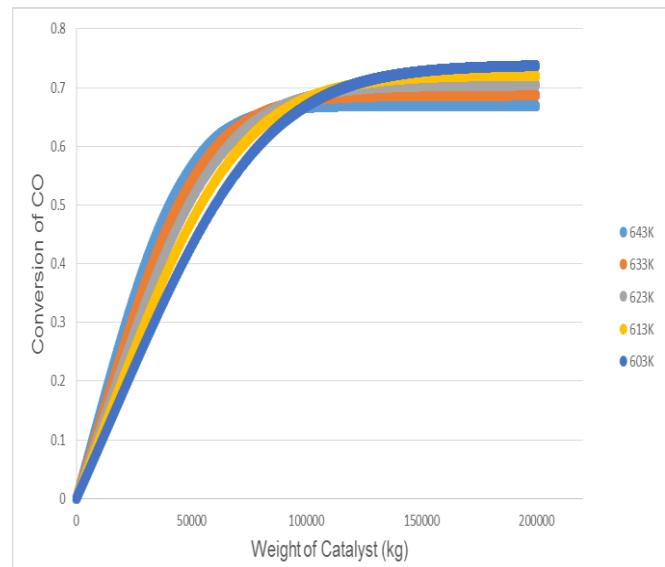


Figure 3.2 Conversion of Carbon monoxide in High temperature WGS converter changing with the weight of catalyst with different feeding temperature.

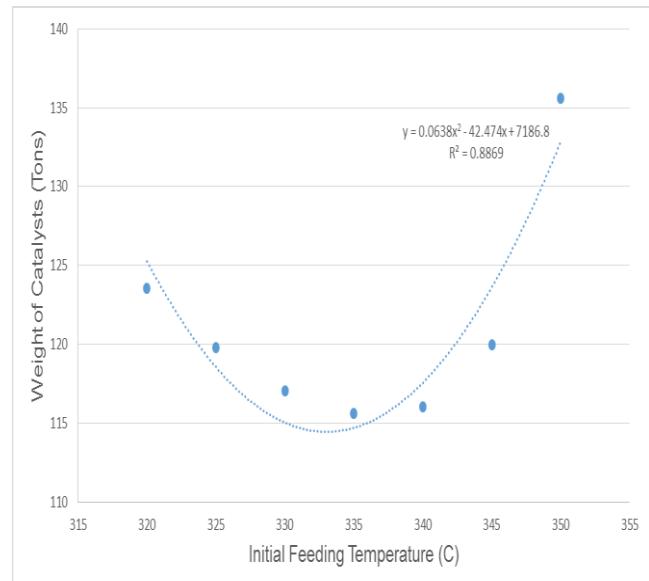


Figure 3.3 Weight of catalysts in relation with initial feeding temperature with a 70.0% conversion for High Temperature WGS Converter.

Based on the information from figure 3.1 and 3.2, it is still ambiguous about the optimal feeding temperature. Therefore, figure 3.3 is generated, this shows the weight of catalysts required for the High temperature WGS reactor to reach a conversion of 70.0% with different feeding temperature. A 70.0% conversion is only used to demonstrate the relation between the feeding temperature and weight of catalyst and how to choose the optimal temperature, this is not necessarily the final choice. The highest feeding temperature it can have is around 350°C because if a higher temperature was used, the reaction will

reach equilibrium before a conversion of 70% can be achieved. A temperature too low cannot be used because the rate of reaction will be too low and it take a long time to reach a conversion of 70.0% despite it gives a higher equilibrium conversion. From the figure, the lowest weight of catalysts required is around 114 tons and it requires a feeding temperature of 333°C, and the end temperature will be 428 °C. The catalysts volume can be calculated based on the weight and the bulk density of the catalysts which is obtained from Rase (1977).

$$V_{High} = \frac{m}{\rho} = \frac{114 \times 10^3}{1250} = 91.2 m^3 \quad (3.1)$$

### 3.2 Low Temperature WGS converter

Same with the High Temperature WGS converter, by changing the feeding temperature, the conversion and the equilibrium temperature will change respectively. This is shown in figure 3.4 and 3.5. A change of 10°C is used.

Figure 3.4 shows the temperature profile in the reactor. Comparing with figure 7.3, there is a significantly smaller change in temperature, which is expected when there is less reactant hence less heat released by the reaction. Even it is less obvious, it still shows that with a higher feeding temperature, the reaction goes to equilibrium faster, which lower the catalysts requirement.

Figure 3.5 shows the conversion changing with the weight of catalysts. The higher the temperature, the quicker the reaction reaches equilibrium. However, higher temperature tends to have a lower conversion at the equilibrium, which is the nature of an exothermal reversible reaction.

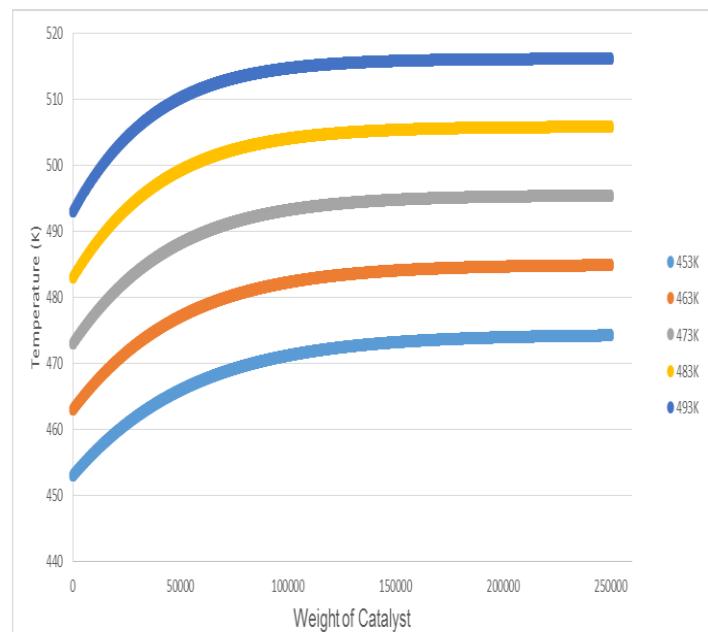


Figure 3.4 Temperature profile in the Low temperature WGS converter, changing with the weight of catalyst with different feeding temperature.

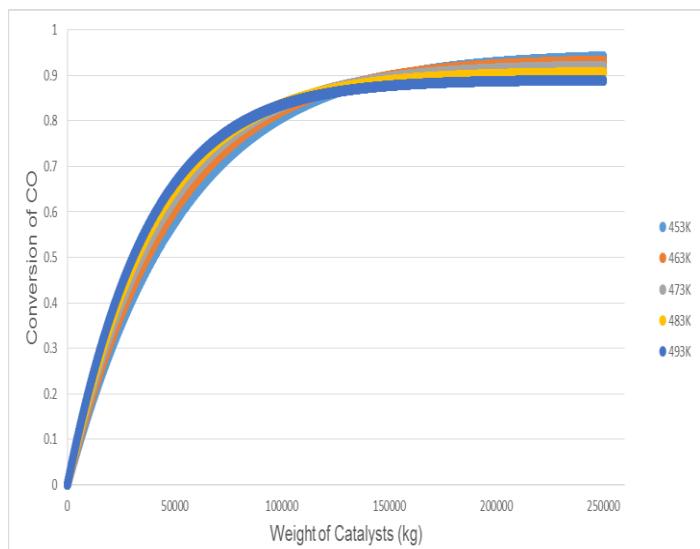


Figure 3.5 Conversion of Carbon monoxide in Low temperature WGS converter changing with the weight of catalyst with different feeding temperature.

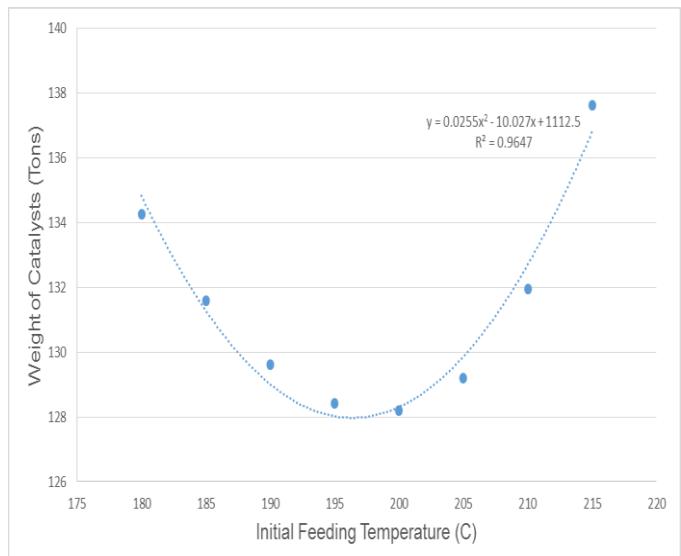


Figure 3.6 Weight of catalysts in relation with initial feeding temperature with an 87.7% conversion for Low Temperature WGS Converter.

Using the same method with the High Temperature WGS converter, figure 3.6 is generated to determine the optimal feeding temperature and the catalysts requirement. For the Low temperature WGS converter, a conversion of 87.7% is used. Based on the figure, the lowest weight of catalysts required is 128 tons and the feeding temperature will be around 197 °C, and the end temperature will be 217 °C. The catalysts volume can be calculated.

$$V_{Low} = \frac{m}{\rho} = \frac{128 \times 10^3}{1442} = 88.77 m^3 \quad (3.2)$$

### 3.3 steam and CO ratio

It is common that the inlet composition of the WGS converters is fixed by the outlet of the secondary reformer, however, additional steam can be added with a different stream which in many cases, will increase the rate of reaction and improve the yield significantly.

High temperature WGS will be taken as an example,  $1\text{ kmol s}^{-1}$  of steam is added each time, the steam and CO ratio is presented on the left of the figure. Based on figure 3.7, there is a dramatic increase in conversion when  $1\text{ kmol s}^{-1}$  of steam is added. In addition, from figure 3.8, there is also an increase on temperature which is expected since the reaction rate increase therefore more heat is released to the system. Figure 3.9 shows the equilibrium conversion changes with the Steam and CO ratio, it increases sharply at the beginning and generally flats out when it reaches a conversion of 90%. Additional steam seems necessary, in addition, the waste heat boiler after the WGS converter can recover most of the heat, and however, steam is expensive, especially with such a high temperature and pressure. It can be argued that there will be an optimal point between a steam ratio of 6 and 10, this will be mainly based on the actual design and the outlet of the secondary reformer.

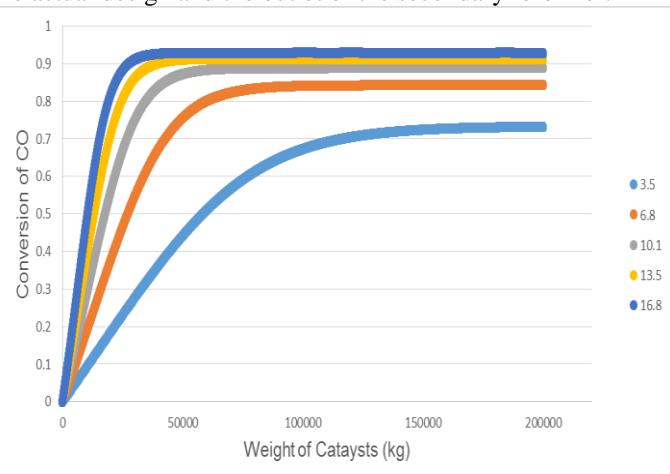


Figure 3.7 Change of steam and CO Ratio in relation with the reactor conversion profile.

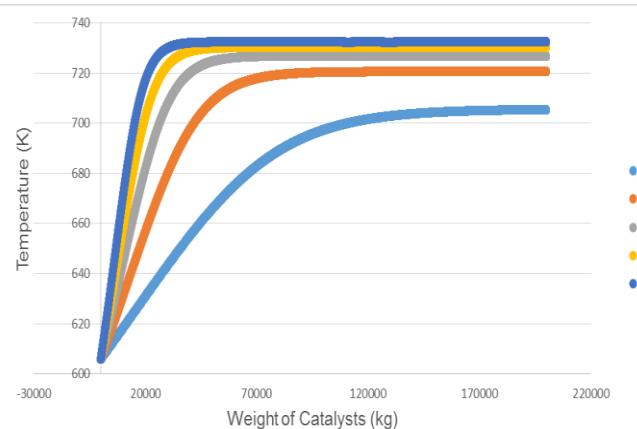


Figure 3.8 Change of steam and CO Ratio in relation with the reactor Temperature profile.

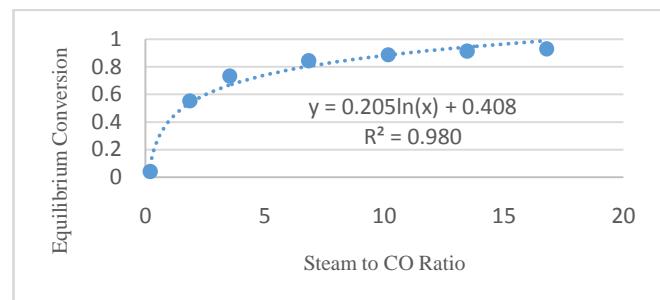


Figure 3.9 Equilibrium conversion in relation to Steam to CO Ratio.

### Conclusion

This is a mathematical model for an adiabatic plug flow reactor which can be used for control, modelling and optimization, even with assumptions, it still gives a good approximation which can be used in a real design. It provides a scope of the design and an optimal operating condition can be chosen.

Not only for WGS converter, but a more generalized model can be developed for other types of reaction and operating condition which enables a more detailed mechanical design and costs estimations.

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